



Short communication

Dimethoxydiphenylsilane (DDS) as overcharge protection additive for lithium-ion batteries

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H I G H L I G H T S

- DDS can dramatically improve the safety of Li-ion batteries during overcharge process.
- No sacrifice on capacity and cycling stability with DDS incorporation.
- Electro-polymerized layer can postpone the voltage rising up during overcharge state.

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The electrochemical properties and working mechanisms of dimethoxydiphenylsilane (DDS) as an electrolyte additive for overcharge protection of lithium ion batteries have been investigated by microelectrode cyclic voltammetry, galvanostatic charge–discharge cycling, and SEM observation on both the cathode and separator of the overcharged cells. DDS can be electrochemically polymerized when the cell was overcharged to 4.9 V (vs. Li/Li⁺), resulting in a polymer layer on the electrode and the separator, which increases the internal resistance of the cell and postpones the voltage rising up during the overcharge process. Therefore, the safety issue of lithium-ion batteries during overcharge state can be significantly improved by utilization of DDS. Furthermore, incorporation of DDS does not significantly degrade the performance of the cell as there is only a small capacity loss during the normal charge–discharge process.

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1. Introduction

Li-ion batteries have the best gravimetric and volumetric energy density of commercially produced rechargeable batteries. Due to the high energy density, Li-ion batteries are being intensively pursued for transportation applications, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and electric vehicles (EV). However, cost, safety, and cycle and calendar life are some of the major obstacles in successfully adopting lithium ion batteries for vehicle applications. In particularly, the safety issue is the most concerning factor for large-scale applications. Cells have

been known to explode and catch fire during overcharge abuse due to several exothermic reactions occurring inside the cell, including oxidation of the electrolyte, and high flammability of the organic solvents of the electrolyte [1,2].

To prevent overcharge, commercial small lithium ion batteries are usually protected with external electronic devices, such as positive temperature coefficient resistor (PTC) or integrated circuits (ICs). However, both remedies add to the manufacturing cost and lead to a lower cell energy density. Most importantly, the safety of the external protection depends on the reliability of the electronic devices.

Therefore, it is essential to develop an internal overcharge protection for lithium ion batteries. In recent years, many efforts have been devoted to the development of internal self-actuating overcharge protection mechanisms for rechargeable lithium batteries [1,3–5]. Redox additives were first reported to control the

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voltage runaway as a shuttle between the cathode and the anode to shut down charge current [6–9]. However, few have been found to work effectively due to the solubility and operating voltage range limits. In addition, most of these redox shuttle additives cause severe capacity loss and self-discharge of the batteries. Additives, such as biphenyl, xylene, cyclohexyl benzene have also been investigated for overcharge protection [1,3]. Those compounds can be electrochemically polymerized on the cathode during the overcharging process. The formed polymer film seems to act as a passivation layer increasing internal impedance and will eventually shut down LIBs although the mechanism is not completely understood. The charge-cutoff potential of most commercial lithium ion batteries is 4.2 V and the oxidative decomposition of the electrolyte being around 5 V. In order to avoid the decomposition of electrolyte, the overcharging protection additives should be polymerized at the potential region between 4.2 and 5 V. If the kinetic effect is considered, the electro-oxidative polymerization of the additives should proceed at a sufficiently high rate in order to provide an effective barrier to prevent the oxidative decomposition of the cathode material and electrolyte. Also, the additives must have little negative effects on normal charge–discharge performance.

In this paper, we investigated the electrochemical properties and safety behaviors of dimethoxydiphenylsilane (DDS) as an overcharge protection additive for lithium-ion batteries, and the impacts on the performance of the battery.

2. Experimental

The electrolyte used in this work was 1 mol L⁻¹ LiPF₆ dissolved in a 1:1:1 mixture (by weight) of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl–methyl carbonate (EMC) (Guangzhou Tinci Materials Co., Ltd., battery grade). The preparation of the electrolyte was conducted in a high purity argon-filled glove box (Braun). The contents of water and free acid (HF) in the electrolyte were kept to below 20 and 50 ppm, respectively, determined by Karl-Fisher 831 Coulometer (Metrohm) for H₂O and Karl-Fisher 798 GPT Titrimo (Metrohm) for HF.

Dimethoxydiphenylsilane (DDS) was purchased from Sigma–Aldrich and was further purified by distillation. The electrochemical behaviors of DDS were studied with cyclic voltammetry (CV) on the Pt microelectrode (diameter = 100 μm) and LiCoO₂ powder microelectrode, respectively. The LiCoO₂ powder was prepared by corroding Pt microelectrode in nitrohydrochloric acid for 30 min to form a micro-cravity at the tip, and then filled the LiCoO₂ powder into the micro-cravity [10,11]. The cyclic voltammetry measurements were recorded on a three-electrode cell using a large lithium sheet as both counter electrode and reference electrode, with a CHI650B electrochemical workstation (Shanghai, China).

Conductivities were measured using a Metrohm 856 conductivity meter using Orion 018010 conductivity cell (the cell constant was about 1 cm⁻¹). The conductivity cell was enclosed in an airtight Ace Glass-Thred glass jacket using Ace-Thred Teflon adapter and FETFE O-ring. The cell contained 6–7 mL of the solution. All the measurements were conducted at room temperature (25 °C). EIS measurements were carried out at discharge state, the AC perturbation was ±10 mV, and the frequency range was from 10⁵ Hz to 10 mHz by using a PGSTAT-30 electrochemical station (Autolab).

The charge–discharge behaviors and cycling performances were investigated using coin cells (2016) with LiCoO₂ as the cathode and lithium disc as the anode. The separator used was Celgard 2400 microporous membrane. The coin cells were charged and discharged at 1/3 C rate in the potential range of 3.6–4.2 V, and then overcharged to 5.0 V at 2/3 C rate using LAND battery cycle

Table 1

Ionic conductivity of the electrolyte with various concentrations of DDS.

Electrolyte	Ionic conductivity (mS cm ⁻¹)
Blank	9.2
2.5% DDS addition	9.1
5% DDS addition	8.4
7.5% DDS addition	7.9

(CT2001A, China). In order to evaluate the influence of DDS on the cycling performance of the batteries, cycling tests were carried out with a constant current of 0.2 C rate between 4.2 and 3.0 V. The overcharge curves of the cells with and without DDS were recorded on Arbin cycler (BT2000) with a constant current of 0.5 C rate.

The morphological changes at both LiCoO₂ electrodes and separators after overcharge were observed by scanning electron microscope (JEOL, JSM-6380LV, Japan).

3. Results and discussion

3.1. Ionic conductivity

Table 1 shows the conductivity of the electrolytes with various concentrations of DDS. The blank electrolyte, 1.0 M LiPF₆ EC/DMC/EMC, the ionic conductivity is 9.2 mS cm⁻¹. With the addition of 2.5, 5, 7.5% DDS, the ionic conductivity of the electrolyte decreases from 9.2 for blank electrolyte to 9.1, 8.4 and 7.9 mS cm⁻¹ for DDS-containing electrolyte. Like other additives for overcharging protection, incorporation of DDS decreases the ionic conductivity of the electrolyte.

3.2. Electrochemical behaviors of DDS on Pt electrode

Fig. 1 shows the linear sweep curves obtained from a Pt microelectrodes in 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1/1/1) without (a) and with (b) 5 wt% DDS at a scan rate of 10 mV s⁻¹. In the electrolyte without DDS, oxidation current appears when the potential reaches 4.6 V, which is attributed to the oxidation of electrolyte on Pt electrode. However in the electrolyte with DDS, different electrochemical behaviors were observed. When the potential is approached 3.5 V, small oxidation current appears and increases very rapidly as the potential becomes more positive with the peak potential at 4.9 V. The small oxidation current can be assigned to

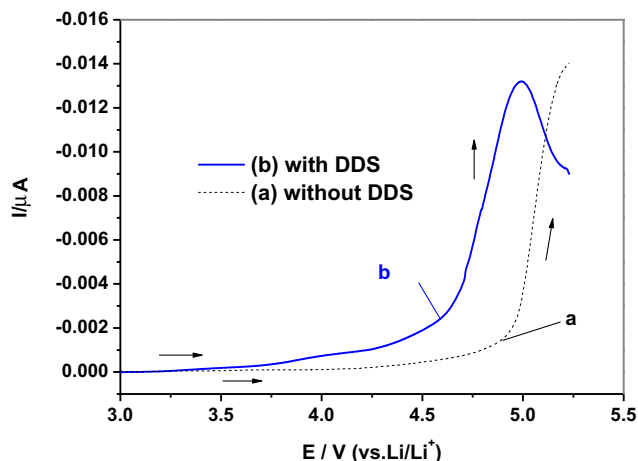


Fig. 1. Linear sweep behaviors of Pt microelectrode in 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1/1/1) without (a) and with (b) 5 wt% DDS, sweep rate 10 mV s⁻¹.

the electro-oxidation of the adsorbed DDS on the Pt electrode, and the large current can be credited to the oxidation of DDS in the electrolyte, which is controlled by diffusion of DDS in the electrolyte [1]. It indicates that dimethoxydiphenylsilane (DDS) has suitable polymerization potential as overcharge protection additive.

3.3. Electro-polymerization behavior of DDS on LiCoO₂ powder microelectrode

Fig. 2 reveals the CV curves of LiCoO₂ powder microelectrode in 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1:1:1) without (a) and with 5% DDS (b) at a scan rate of 0.5 mV s⁻¹. For the electrolyte without DDS, a pair of redox peaks is appeared at about 3.9 V, corresponding to the reversible extracting/insertion of Li-ions from/into LiCoO₂ lattice [12,13]. The electrolyte is dramatically oxidized when the potential reached 5 V as indicated by a significant oxidation peak during the final anodic sweeping process. With regards to the DDS-containing electrolyte, dramatic changes were observed from the CV behavior. The oxidation peak at 3.9 V is related to the extraction of Li-ions from LiCoO₂ occurred during the anodic scan, while the reduction peak at about 3.8 V is corresponding to the insertion of Li-ions into LiCoO₂, which was observed for the electrolyte without DDS, was absent during the cathodic process with DDS. In addition, a huge oxidation peak could be observed at 4.9 V, corresponding to the electro-polymerization on the LiCoO₂ electrode, which is consistent with the electrochemical behavior observed on Pt electrode, as discussed above. The absence of a reduction peak for DDS-containing electrolyte is attributed to the electro-polymerized film, which blocks the insertion of Li-ions into the LiCoO₂ electrode.

3.4. Influence of DDS on overcharge Li/LiCoO₂ cells

In order to evaluate the influence of DDS on the overcharge behavior of a LiCoO₂ electrode, the galvanostatic charge–discharge tests were carried out on Li/LiCoO₂ coin cells. The coin cells were cycled at 1/3 C rate in the potential range of 3.6–4.2 V and followed by overcharging to 5.0 V at 2/3 C rate. It can be seen from Fig. 3 that the initial discharge capacity of the LiCoO₂ electrode in the electrolyte with 5% DDS is 129.2 mAh g⁻¹, very close to the value of 133.5 mAh g⁻¹ observed from the standard electrolyte. This demonstrates that DDS has slightly negative effects on LiCoO₂ electrodes during normal charge–discharge process.

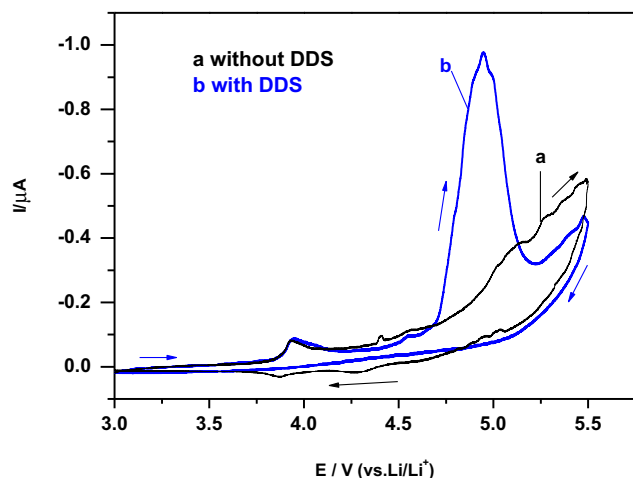


Fig. 2. CV curves of LiCoO₂ powder microelectrode in 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1/1/1) without (a) and with 5% DDS (b), scan rate of 0.5 mV s⁻¹.

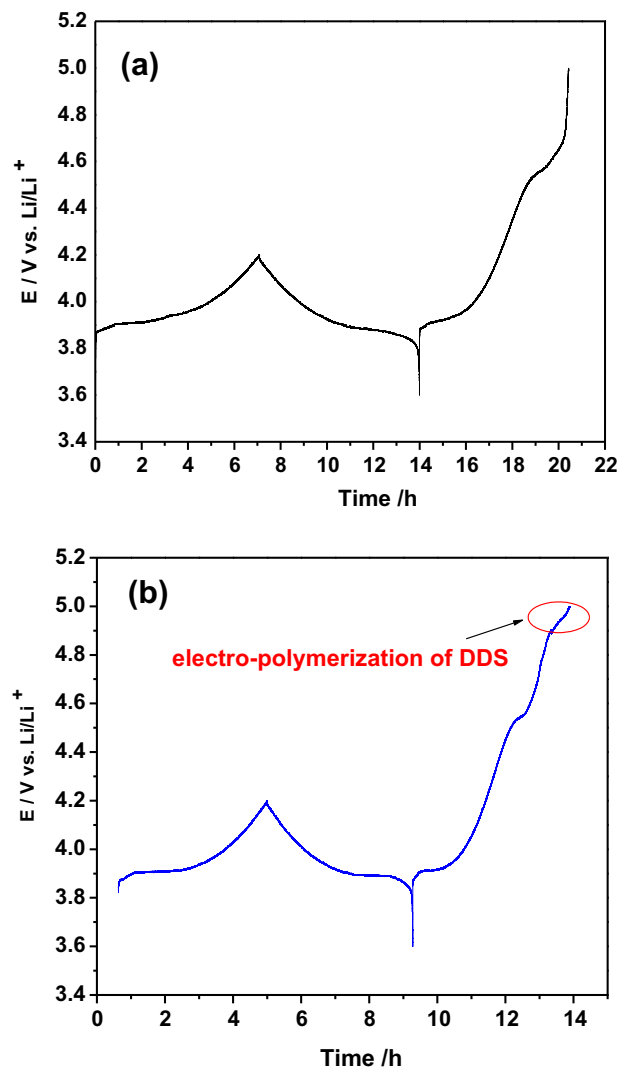


Fig. 3. V–t profiles of Li/LiCoO₂ cells during normal charge–discharge and overcharge with the electrolyte 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1/1/1) with (a) and without 5% DDS (b).

However, dramatic differences of the voltage profiles were found when the cells were undergoing overcharging, as shown in Fig. 3. It is clear that the voltage at overcharged stage rises up sharply to 5 V for the cell without DDS, but a charging voltage plateau of 4.85–5.0 V was observed for the cell with DDS-containing electrolyte, which can be ascribed to the electro-polymerizing of DDS on LiCoO₂ electrode. This suggests that incorporation of DDS to the electrolyte can consume the charge capacity to form a polymerized layer and postpone the sharp voltage rise during the overcharge process. In other words, DDS could be sacrificially polymerized on the cathode surface to enhance the safety of the cell during overcharging. To evidence this assumption, a long period overcharging experiment was conducted, as shown in Fig. 4. The cells with and without DDS were normally charged at a constant current of 0.2 C rate to 4.2 V, followed by overcharged at a constant current of 0.5 C rate. Due to the safety limit of the instrument, the cutoff overcharge potential was set to 5.26 V. As we can see from Fig. 4, with the increasing of overcharging time, the voltage of the cell without DDS rises up rapidly to 5.2 V, and this whole process only takes about 60 min. However, significant difference can be observed for the V–t curve for the cell with 5% DDS containing electrolyte. The voltage of the cell with 5%

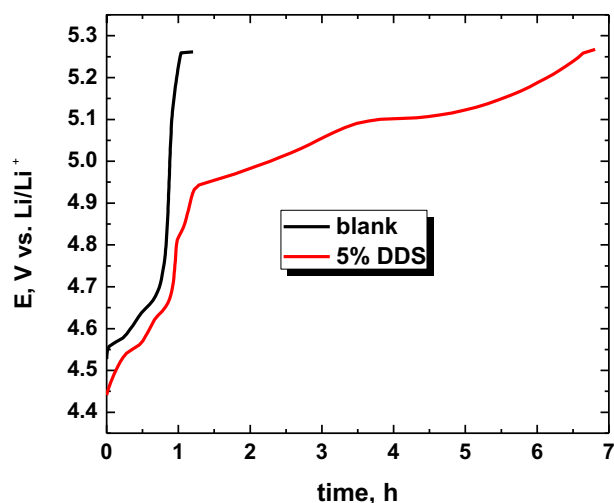


Fig. 4. V–t profiles of Li/LiCoO₂ cells for long period overcharging state with the electrolyte 1.0 M LiPF₆/EC/DMC/EMC (1/1/1) with and without 5% DDS.

DDS containing electrolyte rises up very quick during the initial overcharging state to about 4.9 V, and then takes around 6 h to reach the final cutoff potential. Apparently, the long plateau around 4.9–5.0 V is related to the polymerization of DDS on LiCoO₂ cathode surface. This overcharging result suggests that the incorporation of 5% of DDS can dramatically postpone the growing of potential during the overcharge state and subsequently improve the safety performance.

3.5. SEM images

Fig. 5 shows the morphology of the LiCoO₂ electrodes extracted from the coin cells after being overcharged to 5.0 V. Obviously, for the cell with the standard electrolyte, the bulk structure of primary particles of LiCoO₂ electrode were maintained well after overcharge. In addition, no distinct surface layer was observed. However, as respect to the electrode from the overcharged cell with DDS-containing electrolyte, dramatic changes were found compared to the surface of LiCoO₂ electrode with the blank electrolyte. The surface of LiCoO₂ electrode was found to be coated by a thin film. This deposited film is ascribed to the polymerized derivatives from DDS, as described above.

Fig. 6 compares the SEM images of the separators harvested from the coin cells after being overcharged to 5.0 V. It can be seen from Fig. 6A that the surface of the separator in the blank electrolyte is clear and smooth after overcharging. In contrast, a thin film can be clearly seen on the surface of the separator from the cell with 5% DDS, as seen from Fig. 6B. This phenomenon evidences that the electro-polymerized product not only exists on the cathode but also extends to the separator.

3.6. Electrochemical impedance spectra

Fig. 7 presents the electrochemical impedance spectra of the Li/LiCoO₂ cells with and without 5% additive before and after overcharge. It can be seen that all spectra consisted of a semicircle in the high-to-medium frequency range and a straight line with a slope of about 45° from the real axis in the low frequency range. The high-to-medium frequency semicircle can be attributed to the lithium transport through the surface layers on electrodes, and the low frequency straight line reflects the solid-state Li⁺ diffusion into the active mass [14,15]. Before overcharge, the internal impedance

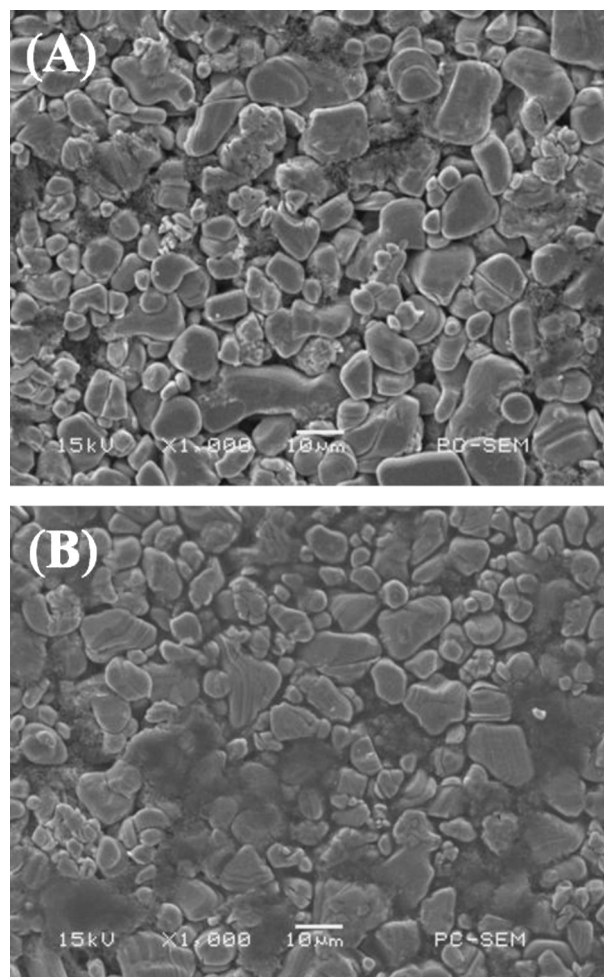


Fig. 5. SEM images of the LiCoO₂ electrodes from the cells after overcharged with the electrolyte 1 mol L⁻¹ LiPF₆/EC/DMC/EMC (1/1/1) without (A) and with 5% DDS (B).

of the cell with DDS is slightly bigger than that without DDS. However, the impedance of the cell with DDS is significantly increased, almost twice than the cell without DDS after overcharge. This supports the conclusion proposed above that a thick polymerized layer was formed on the LiCoO₂ surface, which results in increase in the impedance of surface layer, and therefore postpone the potential rising up during the overcharging state.

3.7. Effects of DDS on electrochemical performance of the LiCoO₂/Li half cell

In order to evaluate the influence of DDS on the cyclic performance of the cells, cycle-life tests were carried out by Li/LiCoO₂ half-cells with a constant current of 0.2 C between 4.2 and 2.5 V. Fig. 8 shows the obtained results. Similar capacity fading trends are observed in Fig. 8. After 35 cycles, the battery without DDS keeps 86.1% of its initial discharge capacity, while the battery with 5% DDS keeps 83.8% of its initial discharge capacity. Although the fading rate of capacity increases with increasing DDS in the electrolyte, this increase is not so significant. The cell with 7.5% DDS keeps 79.4% of its initial discharge capacity after 35 cycles, and coulombic efficiency of the cell is slightly lower than that with the blank electrolyte. This indicates that higher ratio of the DDS might cause lower cyclability and coulombic efficiency.

Fig. 9 shows the charge–discharge curves of the coin cell battery with 5% DDS additive at various charge and discharge rates. It can

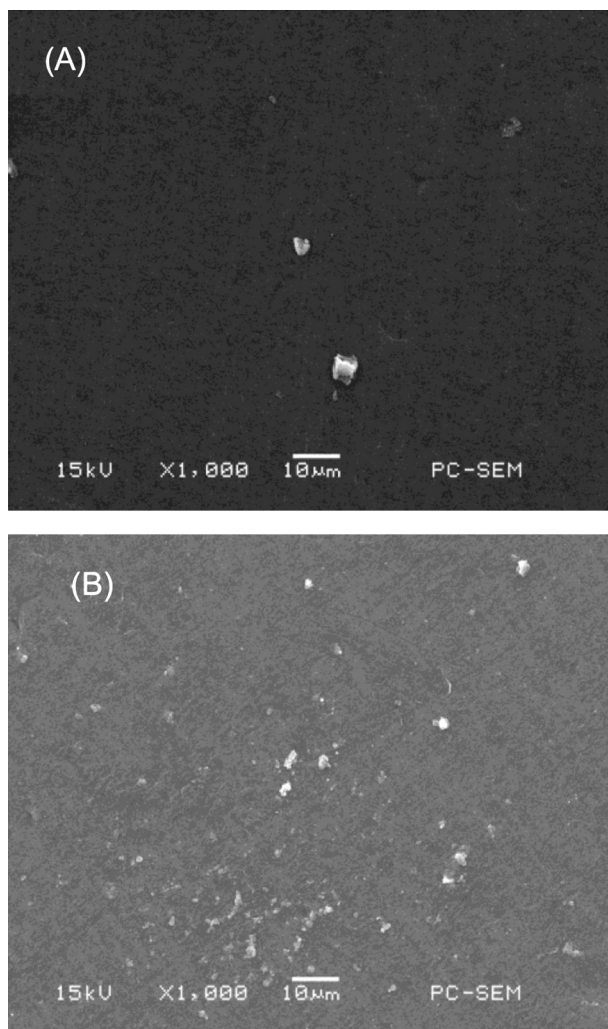


Fig. 6. SEM images of the separators from the coin cells after overcharged with the electrolyte $1 \text{ mol L}^{-1} \text{ LiPF}_6/\text{EC}/\text{DMC}/\text{EMC}$ (1/1/1) without (A) and with 5% DDS (B).

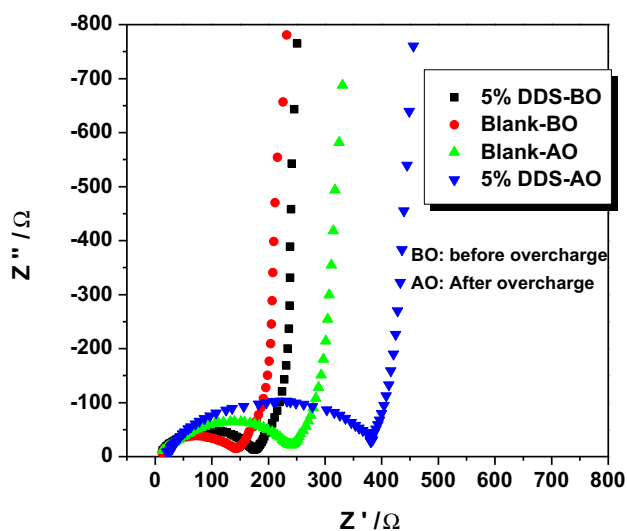


Fig. 7. Electrochemical impedance spectra of Li/LiCoO_2 cells without and with 5 wt% additive before and after overcharge test.

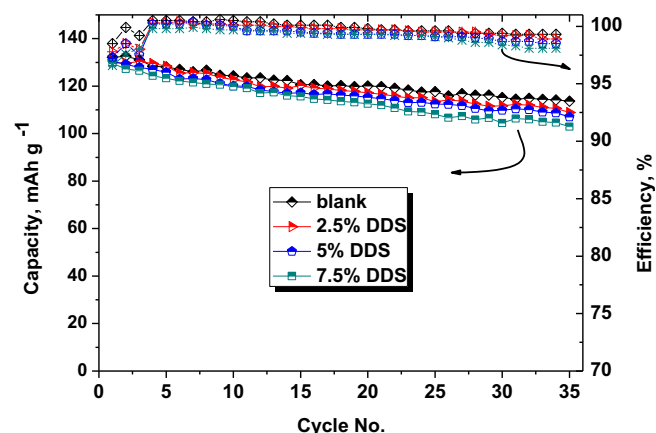


Fig. 8. Effect of DDS on cycling performance of lithium-ion batteries.

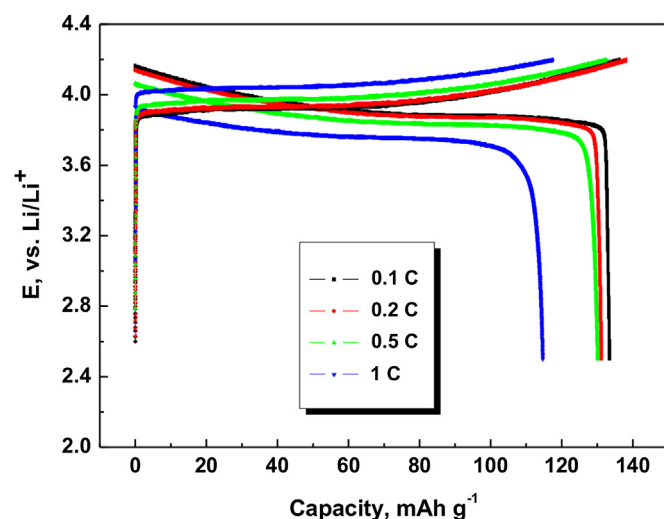


Fig. 9. The charge–discharge curves of the cell using an electrolyte with 5% DDS additive at various charge and discharge rates.

be seen that when the charge rates were increased from 0.1 to 1 C, the charge voltage plateaus of the coin cells decreased slightly. The capacity of the cells remains quite stable from 133.0 to 114.7 mAh g^{-1} , keeping 86.2% of discharge capacity at 0.1 C rate. This indicates the addition of 5% DDS to the electrolyte does not affect the ionic conductivity of the electrolyte.

4. Conclusion

Dimethoxydiphenylsilane (DDS) as an additive was shown to be effective for overcharge protection of Li-ion batteries. DDS was found to electro-polymerize at around 4.8 V on the cathode when the cell overcharged. This formed a polymer film on the cathode and separator, which consumes excess charging current and prevents excessively high voltages during the overcharging state. Electrolyte with high concentrations of DDS showed slightly lower discharge capacity and coulombic efficiency, but these drawbacks could be minimized by using appropriate concentrations of DDS with no compromise on the overcharge protection functionality.

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